# Catalytic Effect of Some Metal Cations on the Reduction of Some Azomethine Compounds

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It has been found that the reducibility of the investigated azomethine compounds is markedly accelerated in presence of $Cd^{++}$ or $Hg^{++}$ ions relative to that $Zn^{++}$, $Sn^{++}$or $Cu^{++}$. The effect of addition of two different metal cations on the reducibility of the studied compounds is also investigated.

Reduction of organic compounds on metals with high hydrogen overvoltage is suggested to take place through an electronic mechanism before protonation(1,2). Azomethins have considerable reducibility at copper cathode(4). The effect of the nature of the surface texture and consequently the hydrogen overvoltage of the cathode on the reducibility of some azomethine compounds is presented here.

## EXPERIMENTAL

The cell and electrolytes are as in proceeding paper(3). Small amounts of (0.001 M) one of the following salts -$Cd^{++}$,$Zn^{++}$,$Sn^{++}$,$Cu^{++}$or $Hg^{++}$was added; Polarization was carried out for about five minutes at 40 mA/cm$^2$ This cathodic treatment allowed the deposition of a thin layer of the metal on the copper cathode. Amalgamated copper cathodes were obtained by amalgamating the copper cathodes in a solution containing $NH_4Cl$ (1 g.) + $HgCl_2$ (1 g.) per litre for 30 seconds.

## RESULTS AND DISCUSSION

The reduction of Benzylidine aniline (I) and p-methoxy benzylidine aniline(II)were carried out in presence of 0.001 M of metal cations. The results are given in Table I. It is found that the addition of 0.001 M $Cd^{++}$ ions to the electroreduction bath markedly increases the reduction efficiency. This behaviour is true for both metallurgical copper and copper amalgam cathodes. The effect of 0.001 M $Hg^{++}$ additions is also found to be noticeable, but lower than that of $Cd^{++}$ions. The effect observed with $Zn^{++}$ and $Sn^{++}$ ions are lower. The effect of the added metal cations can be ascribed to the formation of a very thin microscopic layer of these metals on original cathode. This layer acts as a surface catalyst which is capable of shifting the hydrogen overvoltage to more negative values and increases both potential of zero charge and adsorbability of the organic matter on the surface.These changes are expected to result in an increase in the reducibility of the organic compounds. Even addition of $Cu^{++}$ions is found to affect the reducibility of the investigated Schiff bases probably because of the formation of a more dispersed copper surface. This form of a metal surface enhances the adsorption of organic compounds and consequently decreases the actual current density which leads to a definite increase in the reducibility. It is worthy to note that, in some cases, the effect of the added metal cation differs at different current desities as well as different concentrations of the depolarizers. This behaviour may be due to the different rates at which the metal ion is discharged at the cathode. The addition of two different metal cations (with total concentration 0.001 M) gives, sometimes, higher effects than single cation (c.f. Table 2). This difference in the reducibility caused by one metal cation or two cations can be ascribed to the differences in the surface phase which result in differences in the adsorpability of the depolarizers.

THE CATHODIC POLARIZATION:

The cathodic galvanostatic polarization curves drawn for the effect of some metal cations on the reduction of compound (I) are displayed in figs.1 and 2. Similar results are obtained for compound (II). Generally, the presence of 0.001 M of any of the metal ions, leads to a considerable shift of the cathode potentials to higher negative values. The thin microscopic layer of metal formed increases the hydrogen overvoltage.

$Cu^{++}$ and $Su^{++}$is solution also results in a negative shift of cathodic potential. On the other hand, $Zn^{++}$ ions in solution cause slight shift of the cathode potentials to a less negative values. Actually $Zn^{++}$ions changes the reducibility of the depolarizer least. This may be attributed to the difficulty with which $Zn^{++}$is deposited, specially from such low concentrations (0.001 M). Thus the copper surface is most probably not covered with $Zn^{++}$. Consequently it can be suggested that, $Zn^{++}$ ions participate in the exchange process and the build up of the electric double layer giving rise to the slight change in the cathode potentials and reduction efficiences.

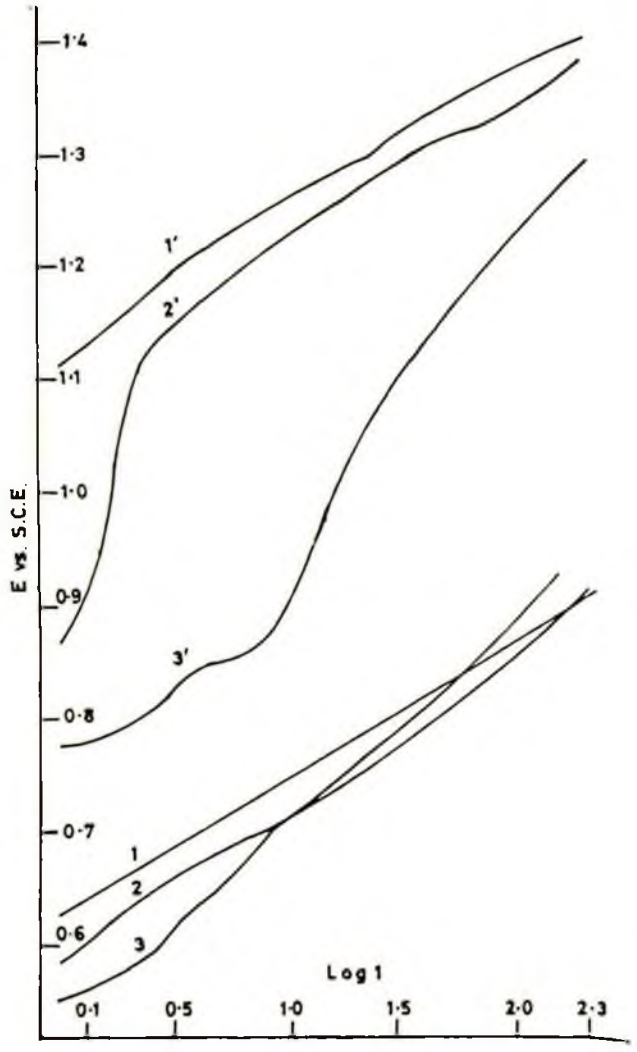



Fig. 1 The cathodic galvanostatic polarisation curves of metallurgical copper cathode for compound I in the presence of Mercury ions (0.001 M), t=31°C, the values on the curves correspond to:
1.1- The hydrogen evolution in the absence of the depolarizer.
2.2- The concentration of the depolarizer 0.10 M
3.3- The concentration of the depolarizer 0.10 M
1.2.3- In the absence of metal cation
1.2.3- In the presence of metal cation

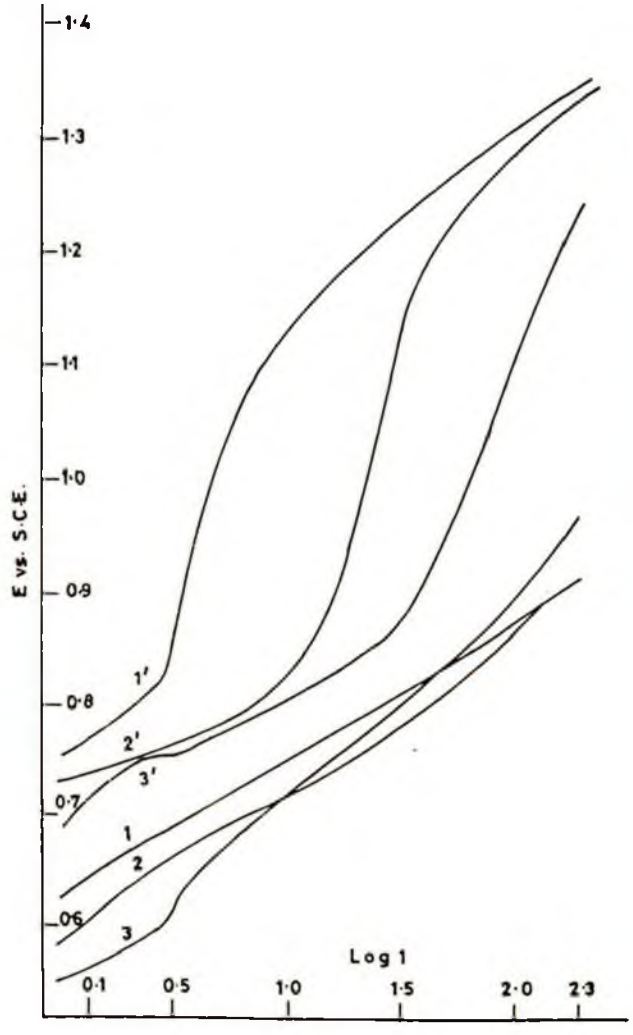



Fig. 2 The cathodic galvanostatic polarization curves of metallurgical copper cathode for compound I, in the presence of cadmium ions(0.001 M), t=31°C, the values on the curves correspond to:
1.1- The hydrogen evolution in the absence of the depolarizer
2.2- The concentration of the depolarizer 0.10 M
3.3- The concentration of the depolarizer 0.10 M
1.2.3- In the absence of metal cation
1.2.3- In the presence of metal cation

## TABLE 1

THE EFFECT OF ADDING 1mM METAL CATIONS ON THE REDUCTION EFFICIENCY (A) OF COMPOUND 1 AT CONCENTRATIONS 0.1 AND 0.01 M AT DIFFERENT CURRENT DENSITIES (t=30°C)

| Cations added | Reduction Efficiency A% | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. bimetallic cations added | | $Cd^{2+}$ | | $Sn^{2+}$ | | $Zn^{2+}$ | | $Cu^{2+}$ | | $Hg^{2+}$ | |
| Conc. of I (M) | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 |
| | on metallurgical copper cathode | | | | | | | | | | | |
| i = 24 mA/cm² | 20.0 | 0 | 45.0 | 5.0 | 15.8 | 0 | 22.5 | 5.0 | 35.0 | 5.0 | 35.0 | 0 |
| 6.0 | 47.4 | 5.0 | 75.0 | 25.0 | 50.0 | 5.0 | 45.0 | 12.5 | 65.0 | 10.0 | 57.9 | 10.5 |
| 0.6 | 90.0 | 22.5 | 80.0 | 53.3 | 76.7 | 33.3 | 87.5 | 25.0 | 100.0 | 20.0 | 90.0 | 25.0 |
| | on copper amalgam cathode | | | | | | | | | | | |
| 24 | 40.0 | 2.50 | 46.1 | 7.7 | 28.2 | 7.7 | 35.0 | 8.0 | - | | | |
| 6.0 | 65.0 | 12.5 | 78.0 | 26.8 | 50.0 | 11.9 | 58.9 | 20.5 | - | | | |
| 0.6 | 97.5 | 25.0 | 90.0 | 45.0 | 83.3 | 26.2 | 82.0 | 28.2 | - | | | |

## TABLE 2

THE EFFECT OF SECOND METAL ION ADDED TO $Cd^{2+}$ (TOTAL CONCENTRATION = 0.001 M) ON THE REDUCTION EFFICIENCY (A%) OF COMPOUND II AT METALLURGICAL COPPER CATHODE POLARIZED AT DIFFERENT CURRENT DENSITIES (t=30°C).

| Metal ion added | Reduction Efficiency A% | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | None | | $Cd^{2+}$ | | $Cd^{2+} + Zn^{2+}$ | | $Cd^{2+} + Cu^{2+}$ | | $Cd^{2+} + Sn^{2+}$ | | $Cd^{2+}$ + amalgam | |
| Conc of II (M) | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 |
| i=24 mA/cm² | 21.0 | 0 | 52.6 | 0 | 28.1 | 9.8 | 50.0 | 10.0 | 27.5 | 15.0 | 65.0 | 12.5 |
| 6.0 | 50.0 | 17.5 | 76.2 | 35.7 | 70.0 | 25.0 | 77.5 | 32.5 | 55.0 | 32.5 | 78.9 | 36.8 |
| 0.6 | 90.0 | 30.0 | 90.2 | 70.7 | 95.0 | 37.5 | 87.5 | 55.0 | 75.0 | 60.0 | 96.0 | 80.0 |

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